Ultrasonic velocity, attenuation, and nonlinearity constant in pure and Cd-doped KCl

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Single crystals of pure and Cd-doped KCl (1000 ppm) were grown by the Czochralski technique. The acoustic attenuation and velocity in pure and Cd-doped KCl for the longitudinal waves along the [100] direction at 12 MHz are measured by single-ended pulse-echo and pulse-echo-overlap methods in the temperature range 173–303 K. The acoustic attenuation is measured in the frequency range 12–228 MHz at room temperature (303 K). The Cd-doped KCl sample showed an increase in attenuation and a decrease in velocity compared to the pure sample. We have also estimated Mason's nonlinearity constant D along the [100] direction at 303 K from the second-order elastic and third-order elastic constants and furthermore used it to evaluate the ultrasonic attenuation in the frequency range 12–228 MHz. These values are compared with our measured attenuation values.

I. INTRODUCTION

It is well known that many useful and important properties of solids have been elucidated by the measurement of attenuation and velocity of ultrasonic waves.[1,2] Although the measurement of sound attenuation is usually emphasized in the literature, information about a physical phenomenon is incomplete without corresponding measurement of sound velocity changes. In almost all phenomena which involve the interaction of sound waves in the medium, both attenuation and velocity are affected. Generally, changes in velocity are small, but the present day techniques have been refined to the extent that the detection of a few parts in 10^8 of velocity changes is possible.[3,4] Measurement of velocity leads to the determination of elastic constants and hence to the lattice vibrational properties and the interatomic forces. The study of acoustic attenuation in solid crystal[5–14] (the cited references are representative, not exhaustive) at high frequencies have attracted the interest of many researchers. We report here the results of measurements of ultrasonic attenuation and velocity along the [100] direction for the longitudinal waves for the pure and Cd-doped (1000 ppm) KCl crystal in the temperature range 170–303 K and frequency dependence in the range 12–228 MHz. It is also our aim to estimate Mason's nonlinearity constant D and hence the ultrasonic attenuation in the Akhieser region for the longitudinal waves along the [100] direction in the frequency range 12–228 MHz.

II. THEORY

A single short duration pulse is introduced into a solid normal to the two parallel faces. A quartz transducer bonded to one of the faces is frequently used for this purpose. Longitudinal and shear waves can be propagated in a solid using X-cut or Y-cut transducers, respectively. Recently, CdS, ZnS, and ZnO have also been successfully used in the thin-film form as the transducer materials. The choice of the bonding material depends on the temperature range to be investigated; phenyl salicylate (salol) and Nonaq stopcock grease are usually used above and below room temperature respectively. The transducer is excited in one of its resonant modes by pulsed high-frequency oscillations. These electrical oscillations are converted into mechanical (elastic) vibrations, which travel back and forth in the solid. In its motion, each time the sound wave impinges on the transducer, a signal is received, which is amplified, demodulated and displayed on a cathode ray oscilloscope screen (Fig. 1). A series of exponentially decreasing echoes are observed. The time interval between successive echoes is the time taken by the sound wave for a round trip in the crystal and hence is related to the velocity of propagation. Knowing the sample thickness, the velocity can be easily found from the relation

$$V = 2l/t \ , \tag{1}$$

where V is the appropriate wave velocity, l the thickness of the sample, and t the time interval between the successive echoes. From the measurement of velocity, the elastic constant S is determined from

$$S = \rho V^2 \ , \tag{2}$$

where ρ is the density of the medium. The attenuation which is a measure of the interaction of the sound wave is given by A,

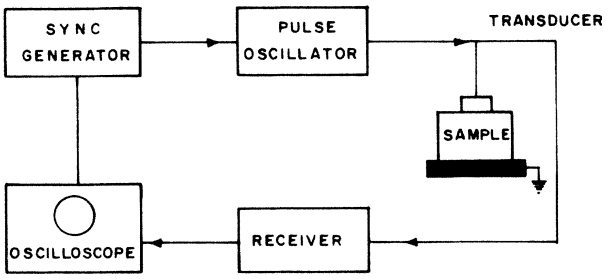

FIG. 1. Simple pulse-echo technique.

$$A\ (\mathrm{dB/cm})=\frac{20}{2l}\log_{10}(h_1/h_2)\ , \tag{3}$$

where h_1 and h_2 are the peak heights of successive echoes. Excellent reviews of the different pulse techniques used in the determination of velocity and attenuation have been given in the literature.[13,15]

The pulse-echo-overlap (PEO) method is a very versatile and highly accurate method for measuring the velocity of ultrasonic waves in materials and structures.[16,17] The absolute accuracy arises from the fact that the method is capable of measuring accurately from any cycle of one echo to the corresponding cycle of the next echo. The PEO method is able to handle diffraction and phase corrections properly and so the absolute accuracy of the PEO method may exceed accuracy of most other methods, even though the precision of some others may exceed that of the PEO method. The details about the principle and measurements are given in the literature.[18,19] The standard method for the measurement of acoustic attenuation was introduced by Roderick *et al.*[20] and later developed by Chick *et al.*[21] and Chung *et al.*[22]

Phonon-phonon interactions give rise to hypersonic losses; the acoustic waves interact directly with individual phonons when the product of the angular frequency ω of the wave and the relaxation time τ is greater than unity. In the Akhieser region,[23] i.e., when $\omega\tau<1$, the attenuation can be successfully accounted for by a theory proposed by Mason,[5] who calculated the effect of strain associated with the waves and arrived at the following expression for attenuation A:

$$A\ (\mathrm{Np/cm})=\frac{E_0(D/3)\omega^2\tau}{2\rho V^3(1+\omega^2\tau^2)}\ , \tag{4}$$

where E_0 is the thermal energy density and D the nonlinearity constant. D is a function of SOEC's and TOEC's (second- and third-order elastic constants) given by

$$D=3\left[\frac{3\sum_i(\gamma_i^j)^2}{n}-\frac{\gamma^2CT_0}{E_0}\right]\ . \tag{5}$$

Here, γ is average Grüneisen number, γ_i^j the Grüneisen numbers associated with different directions and modes, n the number of waves associated with each mode, C the specific heat per unit volume, and T_0 the absolute temperature.

The thermal relaxation time τ_l for the longitudinal wave is evaluated from

$$\tau_l=6K/C\bar{V}^2\ , \tag{6}$$

where K is the coefficient of thermal conductivity and $\bar{V}$ the Debye average velocity given by

$$\frac{1}{\bar{V}^3}=\frac{1}{3}\left[\frac{1}{V_l^3}+\frac{2}{V_s^3}\right]\ , \tag{7}$$

where V_l and V_s are the velocities of longitudinal and shear acoustic waves, respectively.

The elastic constants of alkali-halide crystals have been studied at both low and room temperatures.[24–28] These can be estimated from any force model.[27–30] It has already been shown[31,32] that the effect of doping is to cause a lowering of elastic constants and an increase in the attenuation. When the doping level gets below about 10^{17} impurity atoms per cubic centimeter, the added attenuation and the decrease in velocity get so small that it is not possible to distinguish the effects from phonon-phonon attenuation and thermal changes in velocity.

III. EXPERIMENTAL DETAILS

We grew two single crystals for our measurements in air atmosphere by the Czochralski technique. One crystal was pure KCl and the other was Cd-doped KCl (1000 ppm). The starting material used for this purpose was a seed of KCl. The KCl used for growing the single crystals was analytical reagent manufactured by Glaxo Laboratories and of molecular weight 74.56. The grown crystals were oriented along the [100] direction by cutting them along the cleavage plane. The orientations of both the crystals were less than a degree off and verified by Laue back-reflection technique. The first specimen was a pure crystal, a parallelepiped, 0.9174 cm in thickness, 1.2057 cm in breadth, and 1.2578 cm in length. The other sample was a Cd-doped KCl (1000 ppm) crystal, a parallelepiped of dimension 0.6845 cm in thickness, 1.0482 cm in breadth, and 1.3562 cm in length. By hand lapping the crystals, the opposite faces of the samples were made parallel to each other and were checked by the optikator, and parallelness was found to be better than 3 μm. X-cut transducers of fundamental frequencies of 12 MHz and of size 6 mm in diameter were bonded to one of the faces of the crystal using Nonaq stopcock grease obtained from Dow Corning. This material absorbs moisture, and therefore by heating this material it was made free from water and then carefully bonded. Considerable difficulty has been experienced in measuring the velocity and an attenuation on account of the difference in thermal expansion of quartz transducers and KCl samples. We have used the pure Nonaq stopcock grease for bonding the transducer to the pure KCl crystal. To bond the Cd-doped KCl crystal, just one liquid drop of "ethylene glycol" was used, along with Nonaq stopcock grease to avoid the cracks at low temperatures, which also gave a good sealing with the crystal and transducer. The temperature and frequency range studied were 173–303 K and 12–228 MHz, re-

spectively, for the longitudinal waves. The samples were overlapped by a thin sheet of aluminum (for grounding), except the top surface, and kept properly in the copper sample holder. The cryostat used for the measurement has been reported[33] in the literature. For the velocity and attenuation measurements liquid nitrogen was used to attain the low temperature, measured using a calibrated platinum resistance thermometer. The resistance measurements were carried out using a Datron-1071 Autocal digital multimeter. The ultrasonic attenuation was measured with a pulse echo single-ended technique using a Matec automatic attenuation recorder. Liquid nitrogen was poured in the nitrogen Dewar and the overlapped echoes of interest started shifting to left of the oscilloscope screen. By adjusting the Vernier scale of the cw oscillator, the echoes were again overlapped and the corresponding frequency was noted on a frequency counter for a particular temperature and hence the corresponding ultrasonic velocity. Then the strobe amplitude of the decade divider was turned down and the strobe amplitude of the attenuation recorder was turned up. The attenuation in dB/echo was directly measured and hence the attenuation in dB/cm. This procedure was repeated at different temperatures of interest.

IV. RESULTS AND DISCUSSION

We have measured the ultrasonic velocity and attenuation for the longitudinal waves using a 12-MHz transducer along the [100] direction in the temperature range 173–303 K for pure KCl and Cd-doped KCl crystals. As expected the velocity decreased with the increase in temperature in both the samples and due to doping the velocity is decreased by a small change of 0.20% (Fig. 2). Similarly the ultrasonic attenuation is found to decrease with cooling. However, a small increase in attenuation is observed near 273 K, which may be due to hardening of the seal. Later, a continuous decrease in attenuation with the decrease of temperature is recorded in the range 303–173 K (Fig. 3). The frequency dependence of ultrasonic attenuation in both the samples of KCl crystals at 303 K were measured in the range 12–228 MHz. It is seen that the attenuation increases steeply up to 156 MHz and then drops (Fig. 4). These are probably preliminary measurements of this kind; a more systematic investigation for different doping levels is necessary for a complete understanding.

For completeness we also have calculated Mason's nonlinearity constant D along the [100] direction in a pure KCl crystal. The values of SOEC, TOEC, longitudinal wave velocity V_l, shear wave velocity V_s, the Debye average velocity $\bar{V}$, Debye characteristic temperature, and density ρ have been taken from the literature.[2]

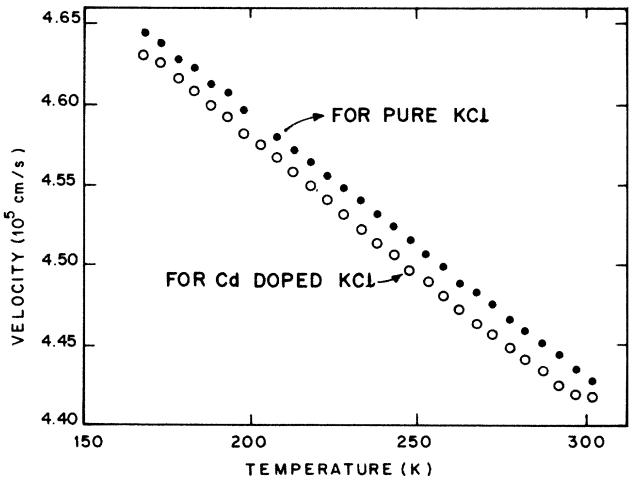

FIG. 2. Comparison of the longitudinal wave velocities in the pure and Cd-doped KCl crystals along the [100] direction at 12 MHz.

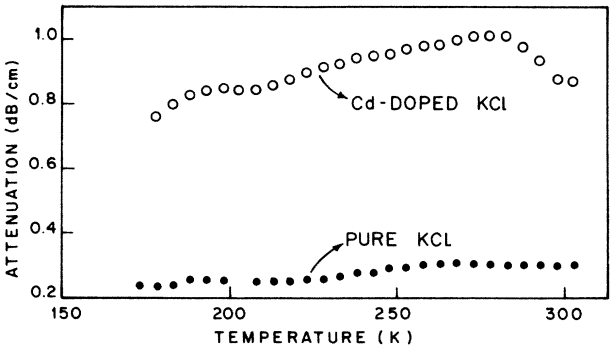

FIG. 3. Temperature dependence of ultrasonic attenuation in the pure and Cd-doped KCl crystals at 12 MHz along the [100] direction for the longitudinal waves.

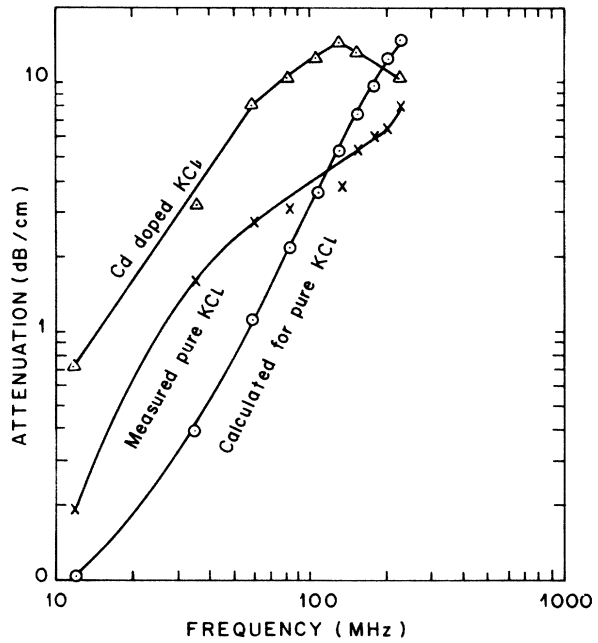

FIG. 4. Frequency dependence of ultrasonic attenuation in the pure and Cd-doped KCl crystal along the [100] direction for the longitudinal waves. ×, measured values for pure KCl; △ measured values for Cd-doped KCl; ⊙, calculated values for pure KCl.

The values of thermal conductivity K, the thermal energy E_0 and the specific heat C have also been taken from the literature.[34] The various primary physical quantities, the numerical values of Grüneisen numbers γ_i^j and average Grüneisen number γ required for the calculation of D and acoustic attenuation have already been reported.[35] The values of the nonlinearity constant D using Eq. (5) and the average Grüneisen number estimated by us are 42.02 and 1.116, which are close to the values available in the literature,[7] 36.06 and 1.38, respectively. The estimated value of $D=42.02$ is being used further to estimate the frequency dependence of ultrasonic attenuation in the Akhieser region in the range 12–228 MHz. A comparison between the measured and estimated values has been shown in Fig. 4. Previously the ultrasonic attenuation had been measured by Lucke[36] and Merkulov.[37] It has been reported by Bonnet *et al.*[38] that usual theories of ultrasonic attenuation (Landu-Rumer and Akhieser) are in disagreement with experiments on NaCl and KCl. They observed a T^n dependence with n approximately equal to 2.8, and an attenuation increasing with the temperature in the low- and high-temperature ranges, respectively, and further proposed an extension of the Landu-Rumer and Akhieser theories at hypersonic frequencies. It is worthwhile to mention that the Mason's nonlinearity constant D is deceptively similar to the nonlinearity parameter β defined by Breazeale and co-workers.[39–42] The nonlinearity constant D is evaluated from the knowledge of the Grüneisen number γ_i^j for various modes and directions and other data, whereas the nonlinearity parameter β is the negative ratio of coefficients of the nonlinear term to the linear term of the (dissipationless) nonlinear wave equation. Both D and β are in general temperature dependent. The Akhieser loss is caused by the relaxational flow of thermal energy between different phonon branches at various temperatures. It is clear that the main contributions to the ultrasonic attenuation in solids are due to phonon-phonon interaction. Hence most of the ultrasonic energy is used in achieving the equilibrium along the various phonon branches and directions.

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